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<b>(54) Title:</b> COEXTRUDED ADHESIVE CONSTRUCTIONS <b>(57) Abstract</b> <p>Die-cuttable and matrix-strippable adhesive constructions and accompanying methods of fabrication are disclosed. The adhesive constructions, which find utility as labels, comprise a coextrudate of a polymeric film (31) and an adhesive layer (30) which may be formed from a thermoplastic elastomer and a tackifier. Additionally, additional layers and release layers (21) may also be incorporated into the adhesive constructions of the invention.</p> <div data-bbox="1010 1129 1360 1335" data-label="Image"> </div>		

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Title: **COEXTRUDED ADHESIVE CONSTRUCTIONS**

**Cross Reference to Related Application**

This application is a continuation-in-part of copending U.S. application serial number 09/148,365 filed September 4, 1998, the written description and claims of which are hereby incorporated by reference in their entirety.

**Field of the Invention**

The present invention relates to thin coextruded adhesive constructions used for making tags, labels, signs, decals and the like and, more particularly, to highly-conformable, cost efficient coextruded pressure-sensitive adhesive constructions.

**Background of the Invention**

Pressure-sensitive adhesive (PSA) constructions such as labels, tapes, decals, signs and the like are known in the art. For example, PSA label constructions are commonly used to apply a particular facestock having a specific nature of printing to an object or article. PSA label constructions typically comprise a release liner, a PSA layer disposed onto the liner, and a facestock laminated onto the PSA layer. This lamination may be formed by first coating or laminating the PSA to the liner, then laminating the facestock onto the PSA-coated liner; or alternatively by coating or laminating the PSA to the facestock, then the PSA-coated facestock onto the liner. The facestock is characteristically made from a web or sheet of paper, cardboard or plastic, which is printed on with information or other indicia either before or after it is laminated to the PSA and liner. In a typical process of "converting" the facestock/PSA/liner laminate, the laminate is printed on the exposed facestock surface, the laminate is die-cut down to the liner surface to outline the label shape, and the waste material between the labels (matrix) is stripped out. The PSA label facestock and adhesive is then adhered to a substrate surface by

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separating the label from the liner and causing the PSA layer of the label to come into contact with the substrate surface. In the most popular labeling process, the label is separated from the liner by bending the liner back over a peel plate, whereupon the label is sufficiently stiff to cause the label to continue on a straight path toward the desired substrate surface.

As used in this patent application, "separation" refers to removal of the label from the liner, "application" refers to adhesion of the label to the substrate surface, and "dispensing" or "dispensability" refers to the combined steps of separation and application. "Peel plate dispensing" denotes the use of a peel plate or other similar device having a small radius of curvature in the separation of liner from label.

The term "faceless" pressure sensitive adhesive constructions is used in the present application to refer to the very thin (e.g., less than 1 mil, preferably 0.1 to 0.5 or 0.6 mils), and to contrast the manufacturing methods disclosed herein from conventional PSA label construction manufacturing methods. As discussed above, in conventional manufacture of PSA label materials, a self supporting preformed web or sheet is laminated to a PSA ("preformed" means that the facestock had been formed into a self supporting web or sheet in a previous manufacturing process, and in the case of a liquid or molten facestock material, that the material has been dried or hardened). Faceless constructions of the present invention are formed by coextrusion of a film forming material (herein sometimes referred to as "FFM") and an adhesive whereby the facestock web or sheet and the adhesive are formed in situ.

In the manufacture and production of PSA constructions, a substantial amount of the overall cost involved is attributed to the material costs for the different material layers, e.g., the PSA and the facestock, be it paper, cardboard, or plastic. The layer thicknesses and layer materials for such conventional PSA constructions have been selected to provide desired properties of convertibility, e.g., by conventional converting techniques such as by die-cutting and matrix-stripping; dispensability, e.g., by conventional dispensing equipment such as by peel plate; and conformability, e.g., enabling the applied

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label to adhere to an irregular or deformable substrate surface without becoming detached or damaged.

5 It is known that the stiffness of a PSA construction will have an impact on its convertibility and dispensability. The stiffness of a label of a given material decreases as the label is made thinner. As a rule of thumb, as the construction stiffness is increased so is convertibility and dispensability of the construction. However, the conformability of a PSA construction is known to decrease as the construction stiffness is increased. Thus, the objective stiffness for a PSA construction is a compromise between convertibility/dispensability and conformability and cost. Too low a stiffness of the label will cause the label to go around the peel plate with the liner. It is one objective of this invention to provide a minimal material label construction with enough stiffness to be dispensable using a peel plate.

15 Prior art PSA constructions having a Gurley stiffness of at least 10 and more commonly of at least 20 or greater are known and are described in U.S. Patent Nos. 5,186,782; 5,516,393; 4,713,273; and 5,451,283. The '782, '393 and '283 patents exploited the idea that a proper differential between machine direction stiffness and cross dimension stiffness, with the latter being the lower of the two, could enable a heat-set film to be dispensed at high speeds, yet be suitable for flexible-film end uses. Such label film might exhibit acceptable overall conformability to flexible substrates even though the film has less inherent conformability than the then standard polymer labels based on polyvinyl chloride (PVC).

25 Specific end uses calling for highly-conformable PSA constructions include those where the label is to be adhered to a small-diameter contoured surface or irregular surface. In such an end use, unnecessary construction stiffness or rigidity could interfere with label's ability to conform and remain adhered to the underlying substrate surface. Additionally, these conventional PSA constructions are not manufactured in a most economically efficient manner.

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5 Additionally, conventional PSA label constructions are not well suited for specific uses such as label uses where the label and underlying substrate are subjected to particular process conditions. For example, conventional PSA label constructions comprising a paper facestock and/or  
10 lacking necessary properties of conformability are known to be adversely affected when used on glass beverage bottles, during the washing/rinsing, filling and pasteurization process, due not only the decomposition of the paper facestock itself but also to the failure of the PSA to remain adhered to the substrate surface. It is believed that such label lifting can be attributed to the rigidity or stiffness of such conventional PSA labels that, once the PSA is heated, causes the label and PSA to peel away and lift from the substrate surface. In this instance, to avoid damage to the paper label, the paper labels are applied to a bottle after it has been rinsed, filled, and pasteurized, i.e., the label is "post applied". Generally, printed paper labels are post applied to filled  
15 bottles using aqueous adhesives or hot melt adhesives.

If post-applied paper labels are not completely adhered to the bottle, are misaligned on the bottle, or are otherwise incorrectly applied to the filled bottle, then the entire bottle and contents will be unusable and must be discarded. Thus, it is desired that glass bottles be labeled and inspected prior  
20 to being filled and pasteurized to eliminate defective bottles or labels.

It is known in the art to use certain high-performance acrylic PSA to pre-apply plastic labels to glass bottles following bottle formation at a bottle manufacturing plant. Examples include Optiflex labels available from Flexcon, and Primeline label films available from Polykote Corporation. While these labels  
25 can generally withstand the bottle washing/rinsing, filling, and pasteurization operations at a bottle filling plant, they make use of specialized adhesives, such as solvent or emulsion acrylics, that are economically undesirable from a manufacturing perspective, making them an unattractive option when compared to conventional gum-type labels.

30 It is, therefore, desired to provide a thin PSA construction for use as a label, tag, decal, sign and the like. In one embodiment, it is desired that

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any printed message or indicia on such construction be protected from damage that can be caused by contact with adjacent physical objects or by exposure to moisture, weather and the like. Also, it is desired that the PSA label construction be convertible by die-cutting and matrix-stripping methods at high speeds, and be highly conformable. It is further desired that such PSA construction be capable of withstanding rinsing, filling, and pasteurization operations when applied to a glass beverage bottle to permit its use as a pre-applied label. Such PSA constructions also are useful in labelling of fruit and in this application, the labels should be resistant to moisture in view of the various transport methods used including floating the labelled fruit in various solutions during sorting, cleaning, etc. It is also desired that the PSA label construction be manufactured in an economically efficient manner when compared to conventional PSA constructions.

#### Summary of the Invention

A die-cutable and matrix-strippable adhesive construction is described which comprises a coextrudate comprising

A. a continuous polymeric film having an upper surface and a lower surface, and a thickness of from about 0.1 mil up to about 1 mil, and

B. an adhesive layer having an upper and lower surface wherein the upper surface of the adhesive layer is adhesively joined to the lower surface of the polymer film, provided that when the adhesive of the adhesive layer comprises a thermoplastic component and a solid tackifier resin component, the thickness of the polymeric film (A) may be up to 1.5 or 2 mils.

The invention also relates to a die-cutable and matrix strippable pressure sensitive adhesive label construction comprising

A. a coextrudate comprising

A-1. a continuous polymeric film having an upper surface and a lower surface, and a thickness of from about 0.1 to about 1 mil,

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A-2. a pressure sensitive adhesive layer having an upper and lower surface wherein the upper surface of the adhesive layer is adhesively joined to the lower surface of the polymeric film, and

5 B. a substrate having a release surface wherein the release surface is in contact with the lower surface of the adhesive layer of the coextrudate provided, however, that when the adhesive of the adhesive layer comprises a thermoplastic elastomer component and a solid tackifier component, the thickness of the polymer film (A) may be up to 2 mils. For some applications, particularly when the thickness of the continuous polymeric films are at the lower end of the ranges specified, the stiffness and other properties  
10 of the construction can be improved by overlaminating another polymer film over the continuous polymer film. Alternatively when the constructions do not have the required stiffness for peel-plate dispensing, hand dispensing and other dispensing techniques described in U.S. Patents 4,217,164, 4,303,461 and  
15 4,896,793 can be used for dispensing the constructions onto a given substrate.

Die-cut labels also are described which are prepared by die-cutting the die-cuttable and matrix-strippable adhesive constructions of the invention, particularly, those adhesive constructions described above which contain the coextrudate in combination with a substrate having a release surface, wherein  
20 the release surface is in contact with a lower surface of the adhesive layer of the coextrudate. Generally, the substrate having a release surface is a release coated liner or carrier. Methods for preparing the adhesive constructions and die-cut labels are also described.

#### Brief Description of the Drawings

25 Fig. 1 is a schematic side elevation of a method of making an adhesive construction of the invention;

Fig. 1A is a cross-sectional side view of an adhesive construction of the invention as prepared in Fig. 1.

Fig. 1B is a cross-sectional side view of another adhesive construction of the invention as prepared in Fig. 1.  
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Fig. 2 is a schematic side elevation of another method of making an adhesive construction of the invention.

Fig. 3 is a cross-sectional side view of an overlaminated adhesive construction of the invention.

5 Fig. 4 is a cross-sectional side view of another overlaminated adhesive construction of the invention.

### Detailed Description of the Invention

The present invention is directed to thin, printable, convertible, dispensable, and conformable coextruded adhesive constructions generally comprising (A) a thin continuous layer of a polymeric film of from about 0.1 mil up to about 1 or 2 mils, and (B) an adhesive layer which is adhesively joined to the lower surface of the polymeric film. A significant advantage of such coextrudates, is that there is provided a technique for forming very thin label construction of a low caliper printable film laminated to a hot melt PSA. Such thin film PSA label constructions are not generally available using conventional manufacturing processes because of the difficulty in handling such thin polymer films which may be as thin as from 0.2 to about 0.5 or 0.6 mil. In one embodiment, the thin continuous layer of polymer film (A) may comprise more than one film layer. Thus, the film (A) may be a multilayer polymeric film containing up to 9 or 10 thin polymer layers or even up to 500 or 1000 polymer film layers.

In a first embodiment, the polymeric film of the coextrudate can be obtained from any polymeric material that is capable of being coextruded with a variety of adhesives, and more particularly, as described below, with pressure sensitive adhesives. For example, it may be desired that the polymeric film material have a solubility parameter that is inconsistent with or incompatible with that of the adhesive to prevent migration between the two layers when coextruded. The polymeric film material also should, when combined with the adhesive layer, provide a sufficiently self-supporting construction to facilitate label dispensing (label separation and application.) Alternatively, when the

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polymeric film combined with the adhesive is not sufficiently self-supporting, an overlamine layer can be applied to the exposed face of the polymeric film to provide additional stiffness and dispensability, as well as other properties as described more fully below. Preferably, the polymeric film material is chosen to provide the construction with the desired properties such as printability, die-cutability, matrix-strippability, dispensability, etc.

The polymeric film materials useful in the coextrudates of the present invention include polystyrenes, polyolefins, polyamides, polyesters, polycarbonates, polyvinyl alcohol, poly(ethylene vinyl alcohol), polyurethanes, polyacrylates, poly(vinyl acetates), ionomers and mixtures thereof. In one preferred embodiment, the polymeric film material is a polyolefin. The polyolefin film materials generally are characterized as having a melt index or melt flow rate of less than 30, more often less than 20, and most often less than 10 as determined by ASTM Test Method 1238.

The polyolefins which can be utilized as the polymeric film material include polymers and copolymers of ethylene, propylene, 1-butene, etc., or blends of mixtures of such polymers and copolymers. Preferably, the polyolefins comprise polymers and copolymers of ethylene and propylene. In another preferred embodiment, the polyolefins comprise propylene homopolymers, and copolymers such as propylene-ethylene and propylene-1-butene copolymers. Blends of polypropylene and polyethylene with each other, or blends of either or both of them with polypropylene-polyethylene copolymer also are useful. In another embodiment, the polyolefin film materials are those with a very high propylenic content, either polypropylene homopolymer or propylene-ethylene copolymers or blends of polypropylene and polyethylene with low ethylene content, or propylene-1-butene copolymers or blend of polypropylene and poly-1-butene with low butene content.

Various polyethylenes can be utilized as the polymeric film material including low, medium, and high density polyethylenes. An example of a useful low density polyethylene (LDPE) is Rexene 1017 available from Huntsman.

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The propylene homopolymers which can be utilized as the polymeric film material in the constructions of the invention, either alone, or in combination with a propylene copolymer as described herein, include a variety of propylene homopolymers such as those having melt flow rates (MFR) from about 0.5 to about 20 as determined by ASTM Test D 1238, condition L. In one embodiment, propylene homopolymers having MFR's of less than 10, and more often from about 4 to about 10 are particularly useful and provide facestocks having improved die-cuttability. Useful propylene homopolymers also may be characterized as having densities in the range of from about 0.88 to about 0.92 g/cm<sup>3</sup>. A number of useful propylene homopolymers are available commercially from a variety of sources, and some useful polymers include: 5A97, available from Union Carbide and having a melt flow of 12.0 g/10 min and a density of 0.90 g/cm<sup>3</sup>; DX5E66, also available from Union Carbide and having an MFI of 8.8 g/10 min and a density of 0.90 g/cm<sup>3</sup>; and WRD5-1057 from Union Carbide having an MFI of 3.9 g/10 min and a density of 0.90 g/cm<sup>3</sup>. Useful commercial propylene homopolymers are also available from Fina and Montel.

Particularly useful polyamide resins include resins available from EMS American Grilon Inc., Sumter, SC. under the general tradename Grivory such as CF6S, CR-9, XE3303 and G-21. Grivory G-21 is an amorphous nylon copolymer having a glass transition temperature of 125°C, a melt flow index (DIN 53735) of 90 ml/10 min and an elongation at break (ASTM D638) of 15. Grivory CF65 is a nylon 6/12 film grade resin having a melting point of 135°C, a melt flow index of 50 ml/10 min, and an elongation at break in excess of 350%. Grilon CR9 is another nylon 6/12 film grade resin having a melting point of 200°C, a melt flow index of 200 ml/ 10 min, and an elongation at break at 250%. Grilon XE 3303 is a nylon 6.6/6.10 film grade resin having a melting point of 200°C, a melt flow index of 60 ml/ 10 min, and an elongation at break of 100%. Other useful polyamide resins include those commercially available from, for example, Union Camp of Wayne, New Jersey under the Uni-Rez product line, and dimer-based polyamide resins available from Bostik, Emery,

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Fuller, Henkel (under the Versamid product line). Other suitable polyamides include those produced by condensing dimerized vegetable acids with hexamethylene diamine. Examples of polyamides available from Union Camp include Uni-Rez 2665; Uni-Rez 2620; Uni-Rez 2623; and Uni-Rez 2695. Some of the physical properties of polymer films formed from the Uni-Rez polyamides are summarized in the following Table I.

Table I

	Uni-Rez Product	Softening Point (°C)	Brookfield Viscosity (cPs at 190°C)	Tensile Strength (PSI)	Percent Ultimate Elongation
10	2620	105	900	1000	50
	2623	106	6500	1000	400
	2665	165	11,000	2000	500
	2695	128	5000	200	175
15	2620/2623 (blend at 1:3)	128	5100	1000	313

Polystyrenes can also be utilized as the polymeric film material in the coextruded adhesive constructions of the invention and these include homopolymers as well as copolymers of styrene and substituted styrene such as alpha-methyl styrene. Examples of styrene copolymers and terpolymers include: acrylonitrile-butene-styrene (ABS); styrene-acrylonitrile copolymers (SAN); styrene butadiene (SB); styrene-maleic anhydride (SMA); and styrene-methyl methacrylate (SMMA); etc. An example of a useful styrene copolymer is KR-10 from Phillips Petroleum Co. KR-10 is believed to be a copolymer of styrene with 1,3-butadiene.

Polyurethanes also can be utilized as the polymeric film material in the coextruded adhesive constructions of the invention, and the polyurethanes may include aliphatic as well as aromatic polyurethanes.

Polyesters prepared from various glycols or polyols and one or more aliphatic or aromatic carboxylic acids also are useful film materials. Polyethylene terephthalate (PET) and PETG (PET modified with cyclohexanedimethanol) are useful film forming materials which are available from a variety of commercial

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sources including Eastman. For example, Kodar 6763 is a PETG available from Eastman Chemical. Another useful polyester from duPont is Selar PT-8307 which is polyethylene terephthalate.

5 Acrylate polymers and copolymers and alkylene vinyl acetate resins (e.g., EVA polymers) also are useful as the film forming materials in the preparation of the coextruded adhesive constructions of the invention. Commercial examples of available polymers include Escorene UL-7520 (Exxon), a copolymer of ethylene with 19.3% vinyl acetate; Nucrell 699 (duPont), an ethylene copolymer containing 11% of methacrylic acid, etc.

10 Ionomers (polyolefins containing ionic bonding of molecular chains) also are useful. Examples of ionomers include ionomeric ethylene copolymers such as Surlyn 1706 (duPont) which is believed to contain interchain ionic bonds based on a zinc salt of ethylene methacrylic acid copolymer. Surlyn 1702 from duPont also is a useful ionomer.

15 Polycarbonates also are useful, and these are available from the Dow Chemical Co. (Calibre) G.E. Plastics (Lexan) and Bayer (Makrolon). Most commercial polycarbonates are obtained by the reaction of bisphenol A and carbonyl chloride in an interfacial process. Molecular weights of the typical commercial polycarbonates vary from about 22,000 to about 35,000, and the melt flow rates generally are in the range of from 4 to 22 g/10 min.

20 The polymeric film material may contain inorganic fillers and other organic or inorganic additives to provide desired properties such as appearance properties (opaque or colored films), durability and processing characteristics. Nucleating agents can be added to increase crystallinity and thereby increase stiffness. Examples of useful materials include calcium carbonate, titanium dioxide, metal particles, fibers, flame retardants, antioxidant compounds, heat stabilizers, light stabilizers, ultraviolet light stabilizers, antiblocking agents, processing aids, acid acceptors, etc.

25 Various nucleating agents and pigments can be incorporated into the films of the present invention. The amount of nucleating agent added should be an amount sufficient to provide the desired modification of the crystal

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structure while not having an adverse effect on the desired properties of the films. It is generally desired to utilize a nucleating agent to modify the crystal structure and provide a large number of considerably smaller crystals or spherulites to improve the transparency (clarity), and stiffness, and the die-cutability of the film. Obviously, the amount of nucleating agent added to the film formulation should not have a deleterious affect on the clarity of the film. Nucleating agents which have been used heretofore for polymer films include mineral nucleating agents and organic nucleating agents. Examples of mineral nucleating agents include carbon black, silica, kaolin and talc. Among the organic nucleating agents which have been suggested as useful in polyolefin films include salts of aliphatic mono-basic or di-basic acids or aryalkyl acids such as sodium succinate, sodium glutarate, sodium caproate, sodium 4-methylvalerate, aluminum phenyl acetate, and sodium cinnamate. Alkali metal and aluminum salts of aromatic and alicyclic carboxylic acids such as aluminum benzoate, sodium or potassium benzoate, sodium betanaphtholate, lithium benzoate and aluminum tertiary-butyl benzoate also are useful organic nucleating agents. Substituted sorbitol derivatives such as bis (benzylidene) and bis (alkylbenzylidene) sorbitols wherein the alkyl groups contain from about 2 to about 18 carbon atoms are useful nucleating agents. More particularly, sorbitol derivatives such as 1,3,2,4-dibenzylidene sorbitol, 1,3,2,4-di-para-methylbenzylidene sorbitol, and 1,3,2,4-di-para-methylbenzylidene sorbitol are effective nucleating agents for polypropylenes. Useful nucleating agents are commercially available from a number of sources. Millad 8C-41-10, (a concentrate of 10% Millad 3988 and 90% polypropylene), Millad 3988 and Millad 3905 are sorbitol nucleating agents available from Milliken Chemical Co.

The amounts of nucleating agent incorporated into the film formulations of the present invention generally range from about 100 to about 6000 ppm of the film. In another embodiment, the amount of nucleating agent is in the range of about 1000 to about 5000 ppm, more preferably of about 1500 to 3500 ppm, more preferably about 2000 to 2500 ppm.

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The polymeric film material is chosen to provide a continuous polymer film in the coextrudate with the desired properties such as improved printability, weatherability, strength, water resistance, abrasion resistance, gloss, die-cutability, matrix strippability and other properties. It is particularly desirable that the surface of the film can be printed or adapted to be printed with inks using printing techniques such as flexographic printing, screen printing, offset lithography, letter press, thermal transfer, etc., and that the applied ink has acceptable adhesion to the surface of the film of the adhesive construction. The choice of polymeric film forming material also is determined by its physical properties such as melt viscosity, high speed tensile strength, percent elongation etc. As will be discussed in more detail below, coextrusion of the polymeric film material and the adhesive to form the coextrudate is facilitated when the melt viscosities of the two materials, i.e., the polymeric film material of the first layer and the adhesive material, are similar. Thus, the choice of polymeric film material to be utilized in the formation of the coextruded adhesive constructions of the present invention may be dependent upon the melt viscosity of the adhesive being coextruded with the polymeric film forming material. In one embodiment, the polymeric film material of the first layer has a hot melt viscosity that is within a factor of from about 0.07 to about 15 times, more often greater than 1 to about 15 times, and preferably from 1 up to about 10 times the hot melt viscosity of the adhesive at the shear rates incurred during the coextrusion process. Generally the shear rates range from about  $100 \text{ sec}^{-1}$  to about  $10,000 \text{ sec}^{-1}$ .

The thickness of the polymer film material is from about 0.1 to about 1.5 or even 2.0 mils. More often the thickness of the film is from about 0.2 to about 1.0 mil. A thickness of about 0.5 mils is particularly useful. The continuous polymeric film may comprise a single layer or the film can be a multilayer film of two or more adjacent coextruded layers. For example the film can comprise one layer of a polyolefin and one layer of a blend of a polyolefin and a copolymer of ethylene and vinyl acetate (EVA). In another embodiment the film comprises three layers, a base or core layer of, for example, a

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polyolefin, and skin layers in both sides of the base or core layer which may be comprised of the same or different polymer blends.

Turning now to the adhesives, the coextrudate constructions of the present invention also include an adhesive layer (hereinafter sometimes referred to as "substrate adhesive") having an upper surface and a lower surface wherein the upper surface of the adhesive layer is adhesively joined to the lower surface of the polymer film. The adhesive may be a heat-activated adhesive, a hot melt adhesive, or a pressure sensitive adhesive (PSA). Adhesives which are tacky at any temperature up to about 160°C (about 320°F) are particularly useful. PSAs which are tacky at ambient temperatures are particularly useful in the coextruded adhesive constructions of the present invention. A variety of conventional PSAs can be utilized provided that the viscosity is or can be modified to be similar to the viscosity of the polymeric film material which is being coextruded with the adhesive. Useful PSA compositions are fluid or pumpable at the temperatures used in the melt processing. Also, the adhesive compositions should not significantly degrade or gel at the temperature employed and over the time required for melt processing and extrusion. Typically, the adhesive compositions have a viscosity of from 1000 poise to 1,000,000 poise at the processing temperature.

The adhesives may generally be classified into the following categories:

Random copolymer adhesives such as those based upon acrylate and/or methacrylate copolymers,  $\alpha$ -olefin copolymers, silicone copolymers, chloroprene/acrylonitrile copolymers, and the like.

Block copolymer adhesives including those based upon linear block copolymers (i.e., A-B and A-B-A type), branched block copolymers, star block copolymers, grafted or radial block copolymers, and the like, and

Natural and synthetic rubber adhesives.

A description of useful pressure-sensitive adhesives may be found in *Encyclopedia of Polymer Science and Engineering*, Vol. 13. Wiley-Interscience Publishers (New York, 1988). Additional description of useful pressure-sensitive



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adhesives may be found in *Encyclopedia of Polymer Science and Technology*, Vol. 1, Interscience Publishers (New York, 1964).

Commercially available pressure-sensitive adhesives are useful in the invention. Examples of these adhesives include the hot melt pressure-sensitive adhesives available from H.B. Fuller Company, St. Paul, Minn. as HM-1597, HL-2207-X, HL-2115-X, HL-2193-X. Other useful commercially available pressure-sensitive adhesives include those available from Century Adhesives Corporation, Columbus, Ohio.

Conventional PSAs, including silicone-based PSAs, rubber-based PSAs, and acrylic-based PSAs are useful. Another commercial example of a hot melt adhesive is H2187-01, sold by Ato Findley, Inc., of Wauwatusa, Wisconsin. In addition, rubber based block copolymer PSAs described in U.S. Patent 3,239,478 (Harlan) also can be utilized in the coextruded adhesive constructions of the present invention, and this patent is hereby incorporated by a reference for its disclosure of such hot melt adhesives.

In one preferred embodiment, the pressure sensitive adhesive utilized in the present invention comprise rubber based elastomer materials such as linear, branched, graft or radial block copolymers represented by the diblock structures A-B, the triblock A-B-A, the radial or coupled structures (A-B)<sub>n</sub>, and combinations of these where A represents a hard thermoplastic phase or block which is non-rubbery or glassy or crystalline at room temperature but fluid at higher temperatures, and B represents a soft block which is rubbery or elastomeric at service or room temperature. These thermoplastic elastomers may comprise from about 75% to about 95% by weight of rubbery segments and from about 5% to about 25% by weight of non-rubbery segments.

The non-rubbery segments or hard blocks comprise polymers of mono- and polycyclic aromatic hydrocarbons, and more particularly vinyl-substituted aromatic hydrocarbons which may be monocyclic or bicyclic in nature. The preferred rubbery blocks or segments are polymer blocks of homopolymers or copolymers of aliphatic conjugated dienes. Rubbery materials such as polyisoprene, polybutadiene, and styrene butadiene rubbers may be

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used to form the rubbery block or segment. Particularly preferred rubbery segments include polydienes and saturated olefin rubbers of ethylene/butylene or ethylene/propylene copolymers. The latter rubbers may be obtained from the corresponding unsaturated polyalkylene moieties such as polybutadiene and polyisoprene by hydrogenation thereof.

The block copolymers of vinyl aromatic hydrocarbons and conjugated dienes which may be utilized include any of those which exhibit elastomeric properties. The block copolymers may be diblock, triblock, multiblock, starblock, polyblock or graftblock copolymers. Throughout this specification and claims, the terms diblock, triblock, multiblock, polyblock, and graft or grafted-block with respect to the structural features of block copolymers are to be given their normal meaning as defined in the literature such as in the *Encyclopedia of Polymer Science and Engineering*, Vol. 2, (1985) John Wiley & Sons, Inc., New York, pp. 325-326, and by J.E. McGrath in *Block Copolymers, Science Technology*, Dale J. Meier, Ed., Harwood Academic Publishers, 1979, at pages 1-5.

Such block copolymers may contain various ratios of conjugated dienes to vinyl aromatic hydrocarbons including those containing up to about 40% by weight of vinyl aromatic hydrocarbon. Accordingly, multi-block copolymers may be utilized which are linear or radial symmetric or asymmetric and which have structures represented by the formulae A-B, A-B-A, A-B-A-B, B-A-B, (AB)<sub>0,1,2...</sub>BA, etc., wherein A is a polymer block of a vinyl aromatic hydrocarbon or a conjugated diene/vinyl aromatic hydrocarbon tapered copolymer block, and B is a rubbery polymer block of a conjugated diene.

The block copolymers may be prepared by any of the well-known block polymerization or copolymerization procedures including sequential addition of monomer, incremental addition of monomer, or coupling techniques as illustrated in, for example, U.S. Patents 3,251,905; 3,390,207; 3,598,887; and 4,219,627. As is well known, tapered copolymer blocks can be incorporated in the multi-block copolymers by copolymerizing a mixture of conjugated diene and vinyl aromatic hydrocarbon monomers utilizing the

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difference in their copolymerization reactivity rates. Various patents describe the preparation of multi-block copolymers containing tapered copolymer blocks including U.S. Patents 3,251,905; 3,639,521; and 4,208,356, the disclosures of which are hereby incorporated by reference.

5           Conjugated dienes which may be utilized to prepare the polymers and copolymers are those containing from 4 to about 10 carbon atoms and more generally, from 4 to 6 carbon atoms. Examples include from 1,3-butadiene, 2-methyl-1,3-butadiene (isoprene), 2,3-dimethyl-1,3-butadiene, chloroprene, 1,3-pentadiene, 1,3-hexadiene, etc. Mixtures of these conjugated dienes also  
10           may be used. The preferred conjugated dienes are isoprene and 1,3-butadiene.

          Examples of vinyl aromatic hydrocarbons which may be utilized to prepare the copolymers include styrene and the various substituted styrenes such as o-methylstyrene, p-methylstyrene, p-tert-butylstyrene, 1,3-dimethylstyrene, alpha-methylstyrene, beta-methylstyrene, p-isopropylstyrene, 2,3-dimethylstyrene, o-chlorostyrene, p-chlorostyrene, o-bromostyrene, 2-chloro-4-methylstyrene, etc. The preferred vinyl aromatic hydrocarbon is styrene.  
15           

          Many of the above-described copolymers of conjugated dienes and vinyl aromatic compounds are commercially available. The number average molecular weight of the block copolymers, prior to hydrogenation, is from about  
20           20,000 to about 500,000, preferably from about 40,000 to about 300,000.

          The average molecular weights of the individual blocks within the copolymers may vary within certain limits. In most instances, the vinyl aromatic block will have a number average molecular weight in the order of about 2000 to about 125,000, and preferably between about 4000 and 60,000. The  
25           conjugated diene blocks either before or after hydrogenation will have number average molecular weights in the order of about 10,000 to about 450,000 and more preferably from about 35,000 to 150,000.

          Also, prior to hydrogenation, the vinyl content of the conjugated diene portion generally is from about 10% to about 80%, and the vinyl content  
30           is preferably from about 25% to about 65%, particularly 35% to 55% when it is desired that the modified block copolymer exhibit rubbery elasticity. The vinyl

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content of the block copolymer can be measured by means of nuclear magnetic resonance.

Specific examples of diblock copolymers include styrene—  
butadiene (SB), styrene-isoprene (SI), and the hydrogenated derivatives  
thereof. Examples of triblock polymers include styrene-butadiene-styrene  
(SBS), styrene-isoprene-styrene (SIS), alpha-methylstyrene-butadiene-alpha-  
methylstyrene, and alpha-methylstyrene-isoprene alpha-methylstyrene.  
Examples of commercially available block copolymers useful as the adhesives in  
the present invention include those available from Shell Chemical Company and  
listed in the following Table II.

Table II

	<u>Kraton</u>	<u>Type</u>	<u>Styrene/Rubber Ratio (w)</u>	<u>Melt Index</u>
	D1101	Linear SBS	31/69	< 1
15	D1107P	Linear SIS	15/85	11
	D1111	Linear SIS	22/78	3
	D1112P	Linear SIS	15/85	23
	D1113P	Linear SIS	16/84	24
	D1117P	Linear SIS	17/83	33
20	D1320X	Multi-arm (SI) <sub>n</sub>	10/90	NA

Vector 4111 is an SIS block copolymer available from Dexco of Houston Texas.

Upon hydrogenation of the SBS copolymers comprising a rubbery  
segment of a mixture of 1,4 and 1,2 isomers, a styrene-ethylene-butylene  
styrene (SEBS) block copolymer is obtained. Similarly, hydrogenation of an SIS  
polymer yields a styrene-ethylene propylene-styrene (SEPS) block copolymer.

The selective hydrogenation of the block copolymers may be  
carried out by a variety of well known processes including hydrogenation in the  
presence of such catalysts as Raney nickel, noble metals such as platinum,  
palladium, etc., and soluble transition metal catalysts. Suitable hydrogenation  
processes which can be used are those wherein the diene-containing polymer  
or copolymer is dissolved in an inert hydrocarbon diluent such as cyclohexane  
and hydrogenated by reaction with hydrogen in the presence of a soluble

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hydrogenation catalyst. Such procedures are described in U.S. Patents 3,113,986 and 4,226,952, the disclosures of which are incorporated herein by reference. Such hydrogenation of the block copolymers which are carried out in a manner and to extent as to produce selectively hydrogenated copolymers having a residual unsaturation content in the polydiene block of from about 0.5% to about 20% of their original unsaturation content prior to hydrogenation.

In one embodiment, the conjugated diene portion of the block copolymer is at least 90% saturated and more often at least 95% saturated while the vinyl aromatic portion is not significantly hydrogenated. Particularly useful hydrogenated block copolymers are hydrogenated products of the block copolymers of styrene-isoprene-styrene such as a styrene-(ethylene/propylene)-styrene block polymer. When a polystyrene-polybutadiene-polystyrene block copolymer is hydrogenated, it is desirable that the 1,2-polybutadiene to 1,4-polybutadiene ratio in the polymer is from about 30:70 to about 70:30. When such a block copolymer is hydrogenated, the resulting product resembles a regular copolymer block of ethylene and 1-butene (EB). As noted above, when the conjugated diene employed as isoprene, the resulting hydrogenated product resembles a regular copolymer block of ethylene and propylene (EP).

A number of selectively hydrogenated block copolymers are available commercially from Shell Chemical Company under the general trade designation "Kraton G." One example is Kraton G1652 which is a hydrogenated SBS triblock comprising about 30% by weight of styrene end blocks and a mid-block which is a copolymer of ethylene and 1-butene (EB). A lower molecular weight version of G1652 is available from Shell under the designation Kraton G1650. Kraton G1651 is another SEBS block copolymer which contains about 33% by weight of styrene. Kraton G1657 is an SEBS diblock copolymer which contains about 13%w styrene. This styrene content is lower than the styrene content in Kraton G1650 and Kraton G1652.

In another embodiment, the selectively hydrogenated block copolymer is of the formula

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wherein       $n = 0$  or  $1$ ;  
                  $o$  is  $1$  to  $100$ ;  
                  $p$  is  $0$  or  $1$ ;

5                each  $B$  prior to hydrogenation is predominantly a polymerized conjugated diene hydrocarbon block having a number average molecular weight of about  $20,000$  to about  $450,000$ ;

                 each  $A$  is predominantly a polymerized vinyl aromatic hydrocarbon block having a number average molecular weight of from about  $2000$  to about  
10                 $115,000$ ; the blocks of  $A$  constituting about  $5\%$  to about  $95\%$  by weight of the copolymer; and the unsaturation of the block  $B$  is less than about  $10\%$  of the original unsaturation. In other embodiments, the unsaturation of block  $B$  is reduced upon hydrogenation to less than  $5\%$  of its original value, and the average unsaturation of the hydrogenated block copolymer is reduced to less  
15                than  $20\%$  of its original value.

                 The block copolymers may also include functionalized polymers such as may be obtained by reacting an alpha, beta-olefinically unsaturated monocarboxylic or dicarboxylic acid reagent onto selectively hydrogenated block copolymers of vinyl aromatic hydrocarbons and conjugated dienes as described  
20                above. The reaction between the carboxylic acid reagent in the graft block copolymer can be effected in solutions or by a melt process in the presence of a free radical initiator.

                 The preparation of various selectively hydrogenated block copolymers of conjugated dienes and vinyl aromatic hydrocarbons which have  
25                been grafted with a carboxylic acid reagent is described in a number of patents including U.S. Patents  $4,578,429$ ;  $4,657,970$ ; and  $4,795,782$ , and the disclosures of these patents relating to grafted selectively hydrogenated block copolymers of conjugated dienes and vinyl aromatic compounds, and the preparation of such compounds are hereby incorporated by reference. U.S.  
30                Patent  $4,795,782$  describes and gives examples of the preparation of the

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grafted block copolymers by the solution process and the melt process. U.S. Patent 4,578,429 contains an example of grafting of Kraton G1652 (SEBS) polymer with maleic anhydride with 2,5-dimethyl-2,5-di(t-butylperoxy) hexane by a melt reaction in a twin screw extruder. (See Col. 8, lines 40-61.)

5                Examples of commercially available maleated selectively hydrogenated copolymers of styrene and butadiene include Kraton FG1901X, FG1921X, and FG1924X from Shell, often referred to as maleated selectively hydrogenated SEBS copolymers. FG1901X contains about 1.7%w bound functionality as succinic anhydride and about 28%w of styrene. FG1921X  
10                contains about 1%w of bound functionality as succinic anhydride and 29%w of styrene. FG1924X contains about 13% styrene and about 1% bound functionality as succinic anhydride.

                 Useful block copolymers also are available from Nippon Zeon Co., 2-1, Marunochi, Chiyoda-ku, Tokyo, Japan. For example, Quintac 3530 is  
15                available from Nippon Zeon and is believed to be a linear styrene-isoprene-styrene block copolymer.

                 The polymer film materials and adhesive compositions used to form the constructions of the present invention may be neat, or they may be emulsions or solvent-based. Emulsion and solvent-based acrylic based PSAs are  
20                known and described in, for example, U.S. Patent No. 5,639,811 and 5,164,444, respectively, and these patents are hereby incorporated by reference for such disclosures. When emulsions of the film materials and/or adhesive compositions are used, the water may be removed in an extruder by using the process described and claimed in U.S. Patent 5,716,669 (LaRose et al). It is  
25                preferred, however, that the film materials and PSAs which are coextruded are compositions substantially free (e.g., less than 1%w) of water and/or solvents. The presence of water or solvents during the coextrusion process can result, and generally does result, in pinholes and bubbles in the coextruded film. The presence of voids in the film due to steam is referred to in the art as "moisture  
30                slits."

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Since the adhesive constructions of the present invention are formed by coextruding a film of the above described polymeric film materials and an adhesive layer as described more fully below, the hot melt viscosity of the polymeric film material and of the adhesive should be within a window or range of viscosities which can produce a coextrudate of continuous and uniform layers of the polymeric film material and the adhesive in order to avoid film defects and intermingling of the polymeric film material and the adhesive during the coextrusion process. Intermingling of the film material and the adhesive is not desired because it can cause a loss of clarity in the extruded film, as well as a tendency to cause blocking. In general, it is preferred that the polymeric film material have a hot melt viscosity that is within a factor of from about 0.07 to about 15 times the hot melt viscosity of the adhesive at the shear rates incurred during the coextrusion process. Generally the shear rates range from about 100  $\text{sec}^{-1}$  to about 10,000  $\text{sec}^{-1}$ . More often the factor is from about 1 to about 15. A preferred factor is from 1 to about 10. It is also desirable for the polymer film material and the adhesive to have relatively similar melt viscosities at the extrusion temperatures. For example, when the PSA is a conventional hot melt adhesive, the extrusion temperatures of the PSA are in the range of from about 150°C to about 200°C, and preferably in the range of from about 175°C to about 200°C. It is, therefore, desired that the polymeric film material selected for use with the PSA have an extrusion temperature below about 200°C and preferably in the range of from about 150°C to about 180°C.

It is desired that the continuous polymeric film in the adhesive constructions of the invention have a high speed tensile strength of at least 1 pound/inch-width and more often, a high speed tensile strength in the range of from about 2 to about 10 pounds/inch-width. High speed tensile strength is determined in accordance with TAPPI Test 494 modified by running the sample at a speed of 100 ft/min. The high speed tensile strength of the polymer film should be sufficient, at the given thickness, to permit matrix stripping after die-cutting without undue tearing of the film. It is also desirable that the polymeric film material in the coextruded adhesive constructions of the present invention



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have an elongation at break of less than about 200%, and more preferably, in the range of from about 125% to about 175%. A polymeric film material having a percent ultimate elongation at break greater than about 200% can produce an adhesive construction that is difficult to convert by die-cutting and matrix-stripping, depending on the type of adhesive and polymeric film material, and on their respective coating weights.

In one embodiment, the key features of the coextruded adhesive constructions of the present invention include (1) the use of a thin polymeric film and (2) an adhesive layer having a relatively low coat weight. Thus, the adhesive constructions of the present invention are characterized as having a polymeric film with a thickness of from about 0.1 mil up to about 1.5 or 2 mils, and an adhesive coating weight of less than 40, and preferably less than 20 g/m<sup>2</sup>. In one embodiment, the adhesive layer has a coat weight in the range of from about 0.5 to about 20 g/m<sup>2</sup>. Alternatively, the thickness of the adhesive layer may range from about 0.02 mils to about 2 mils, and more preferably, between about 0.02 mils and about 0.8 mils. It should be understood that the thickness and coat weight of both the polymer film and the adhesive layer may vary depending upon the different types of polymer film material and adhesives that are selected, and the properties desired in the adhesive construction. For example, different polymers and different film thicknesses will result in constructions having different conformabilities and different stiffnesses. The constructions of the invention, in one embodiment, should have sufficient Gurley stiffness to permit high speed dispensing such as by a peel-plate, yet be sufficiently flexible to be conformable to most surfaces. For applications requiring a high degree of conformability, the adhesive constructions can be designed to have Gurley stiffnesses in the machine direction of less than about 10, and even less than about 5. Gurley stiffness is determined according to TAPPI Test 543 pm. Typically, the adhesive constructions of the invention have a Gurley stiffness in the machine direction of less than 40 mg and even less than 25 mg.

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It is also a feature of the coextruded adhesive construction of the present invention that such thin polymeric films can provide the structural properties (e.g., strength and stiffness) necessary to facilitate conversion. The coextruded adhesive constructions of the present invention having a polymeric film of the given thicknesses provides an adhesive construction that is, in combination with the adhesive layer, sufficiently self supporting to facilitate conversion (i.e., printing, die-cutting and matrix stripping). As noted herein, when the machine direction stiffness of the coextruded adhesive constructions is too low (e.g., less than 10 Gurley) to be used satisfactorily in high speed peel-plate dispensing techniques, the construction can be dispensed using other techniques or the stiffness can be increased by overlaminating a polymer film to the thin polymer films of the coextruded adhesive construction as described herein. Useful dispensing techniques and dispensing equipment for adhesive constructions of low stiffness including the Ventura dispenser are described in U.S. Patents 4,217,164, 4,303,461 and 4,896,793, and these patents are incorporated herein for such descriptions.

As mentioned above, in one embodiment, the adhesive compositions comprise thermoplastic elastomers comprising at least one thermoplastic elastomeric block copolymer which include linear, branched, graft or radial block copolymers. In addition, the adhesive compositions which are coextruded also contain at least one solid tackifier resin component. A solid tackifier is defined herein as one having a softening point above 80°C. When the solid tackifier resin component is present, the coextrudable pressure-sensitive adhesive compositions generally comprise from about 40 to about 80% by weight of a thermoplastic elastomer component and from about 20% to about 60% by weight (preferably from about 55 to 65% by weight) of a solid tackifier resin component. The solid tackifier reduces the modulus of the mixture sufficiently to build tack or adhesion. Also, solid tackifiers (particularly the higher molecular weight solid tackifiers (e.g., Mw greater than 2000) and those having a lower dispersity ( $M_w/M_n$  = less than about 3)) are less sensitive to migration into the polymer film layer, and this is desirable, since migration of

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tackifier into the polymer film layer causes dimensional instability, and the constructions can swell and/or wrinkle, and may become too soft. In addition, the constructions may lose adhesive properties or cause blocking, and the ability of the polymer film to be printed satisfactorily may be reduced by migration of the tackifier. For example, attempts to print the polymeric film layer after migration of tackifier or other components from the adhesive layer may result in poor anchorage of the ink and/or blurring of the printing. Migration of the tackifier and other components present in the adhesive layer is a particular problem when the polymer film comprises a polyolefin such as polyethylene.

Conventional solid tackifier resins include hydrocarbon resins, rosin, hydrogenated rosin, rosin esters, polyterpene resins, and other resins which exhibit the proper balance of properties. A variety of useful solid tackifier resins are available commercially such as terpene resins which are sold under the trademark Zonatac by Arizona Chemical Company, and petroleum hydrocarbons resins such as the resins sold under the trademark Escorez by Exxon Chemical Company. One particular example of a useful solid tackifier is Escorez 2596 which is a C<sub>5</sub>-C<sub>9</sub> (aromatic modified aliphatic) synthetic tackifier having an Mw of 2100 and a dispersity (Mw/Mn) of 2.69. Another useful solid tackifier is Escorez 1310LC, identified as an aliphatic hydrocarbon resin having an Mw of 1350 and a dispersity of 1.8. Wingtack 95 is a synthetic tackifier resin available from Goodyear, Akron, Ohio consisting predominantly of polymerized structure derived from piperylene and isoprene.

The modulus of the adhesive mixtures to be coextruded also may be lowered by the incorporation of liquid rubbers, i.e., liquid at room temperature. The liquid rubbers generally will have an Mw of at least 5,000 and more often at least 20,000. Incorporation of liquid rubbers in amounts of less than 10%, and even less than 5% by weight based on the overall weight of the adhesive formulation results in adhesives which is coextrudable with the polymeric film materials. The incorporation of a liquid rubber also produces an adhesive having increased tack and adhesion. Liquid block copolymers such as liquid styrene-isoprene block copolymers are particularly useful. For example,

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Kraton LVSI-101, available from the Shell Chemical Company, is effective in lowering the modulus of the adhesive, and it has been found, surprisingly, that this liquid styrene-isoprene block copolymer functions as a processing aid, improving the smoothness of the flow of the adhesive from the die. Kraton LVSI-101 has a weight average molecular weight of about 40,000. Another example of a useful liquid rubber is a liquid polyisoprene obtained by selectively or partially degrading a high molecular weight polyisoprene. An example of a commercially available partially degraded high molecular weight polyisoprene is Isolene D-400 from Elementis Performance Polymers, Belleville, N.J., and this liquid rubber has an Mw of about 20,000. Other liquid rubbers which may be incorporated into the adhesive mixture include liquid styrene-butadiene rubbers, liquid butadiene rubbers, ethylene-propylene rubbers, etc.

The adhesive compositions also may include other materials such as antioxidants, heat and light stabilizers, ultraviolet light absorbers, viscosity modifiers, fillers, colorants, antiblocking agents, reinforcing agents, processing acids, etc. Hindered phenolic and amine antioxidant compounds may be included in the adhesive compositions, and a wide variety of such antioxidant compounds are known in the art. A variety of antioxidants are available from Ciba-Geigy under the general trade designations "Irganox" and "Irgafos". For example, the hindered phenolic antioxidant n-octadecyl 3-(3,5-di-t-butyl-4-hydroxyphenyl)-proprionate is available under the general trade designation "Irganox 1076". Irganox 1010, is identified as Tetrakis (methylene 3-(3',5'-di-tert-butyl-4'-hydroxyphenyl) proprionate) methane. Irgafos 168 is another useful antioxidant from Ciba-Geigy.

Hydroquinone-based antioxidants also may be utilized, and one example of such an antioxidant is 2,5-di-tertiary-amyl-hydroquinone.

Light stabilizers, heat stabilizers, and UV absorbers also may be included in the adhesive compositions. Ultraviolet absorbers include benzotriazol derivatives, hydroxy benzyl phenones, esters of benzoic acids, oxalic acid, diamides, etc. Light stabilizers include hindered amine light stabilizers, and the

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heat stabilizers include dithiocarbamate compositions such as zinc dibutyl dithiocarbamate.

5 The adhesive compositions, like the polymeric films, may contain inorganic fillers and other organic and inorganic additives to provide desired properties. Examples of useful fillers include calcium carbonate, titanium dioxide, metal particles, fibers, etc. An example of a useful end-block reinforcing agent is Cumar LX509 from Neville Resins.

10 The following examples illustrate specific pressure sensitive adhesive formulations which are coextrudable with polymeric film materials as described above. Unless otherwise indicated in the following examples, in the claims, and elsewhere in the written description, all parts and percentages are by weight, and temperatures are in degrees centigrade.

Adhesive 1		Percent By Weight
15	Kraton D1320X	60.0
	Escorez 2596	40.0
Adhesive 2		
20	Kraton D1320X	57.1
	Escorez 2596	38.1
	Kraton LVSI-101	4.8
Adhesive 3		
25	Kraton D1320X	50.0
	Escorez 2596	45.8
	Kraton LVSI-101	4.2
Adhesive 4		
25	Quintac 3530	50.0
	Escorez 2596	45.8
	Kraton LVSI-101	4.2

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## Adhesive 5

Quintac 3530	50.0
Escorez 2596	45.8
Isolene D-400	4.2

## 5 Adhesive 6

Kraton D1112P	35.0
Escorez 1310LC	65.0

## Adhesive 7

10 Kraton D1117P	35.0
Escorez 1310LC	65.0

## Adhesive 8

Kraton D1112P	35.0
Escorez 2596	65.0

## Adhesive 9

15 Kraton D1107	30.0
Escorez 2596	48.0
Kraton LVSI-101	22.0

## Adhesive 10

20 Vector 4111	52.6
Wingtack 95	31.6
Cumar LX509	15.8

As noted above, the adhesive constructions of the present invention comprise coextrudates of a polymeric film and an adhesive layer. The polymeric film may comprise one or more layers.

25 A coextrusion technique useful in preparing an embodiment of the adhesive constructions of the present invention is schematically shown in Fig. 1. The apparatus shown in Fig. 1 utilizes three extruders 10, 11 and 12 which can provide three molten streams (sometimes hereinafter referred to as streams A, B and C respectively) of material to the coextrusion die 17. Extruder 30 provides a molten stream 13 of an adhesive composition to the die 17. Extruder

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11 provides a molten stream 14 of polymeric film material to the die 17. Extruder 12 is optional, and when present, provides a molten stream 15 of a polymeric film material which may be the same as or different from the polymer film material of molten stream 14 from extruder 11. It is of course understood  
5 that if no third molten stream is desired, there is no need to utilize extruder 12. When extruder 12 is utilized, and the molten stream 15 is a polymer film material which is the same as the polymer film material of molten stream 14, the resulting coextrudate is a two layer construction, one layer of polymer film and one layer of adhesive. When the polymeric film material of molten stream  
10 15 is different from the polymeric film material of molten stream 14, the polymeric film of the coextrudate 23 comprises two layers (31 and 31A in Fig. 1B), and the coextrudate comprises three layers, the two polymer film layers (31 and 31A) and the adhesive layer 30. Additional extruders can be used when it is desired to have additional streams of molten material fed to the die 17. Two  
15 or more extruders containing the same polymeric film material are used to provide a coextrudate with a thicker polymeric film.

In one preferred embodiment, polymer film material is not charged to extruder 12, or the polymer charged to extruder 12 is the same as that charged to extruder 11, and the resulting coextrudate comprises a single layer  
20 of polymer film, and a layer of adhesive.

The extruders 10, 11 and 12 are utilized to blend and melt the compositions and as pumps to deliver the molten streams to the feedblock and the extrusion die. Alternatively, the compositions may be preblended prior to being introduced into the extruders. The precise extruder utilized is not critical  
25 to the process. A number of useful extruders are known, and these include single and twin-screw extruders, batch-off extruders, etc. Such extruders are available from a variety of commercial sources including Killion Extruders, Inc., C.W. Brabender Inc., American Leistritz Extruder Corp, and Davis Standard Corp.

30 A variety of useful coextrusion die systems are known. Examples of extrusion dies useful in the invention are the Cloeren "vane" dies, and

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multimanifold dies available commercially from the Cloeren Company of Orange, Texas.

Although the selection of the extrusion die to be utilized in the process of the invention is not critical, certain factors do have an influence on the performance of the extrusion process. For example, when a single manifold is to be utilized, the relative viscosities of the materials, and their ability to be processed at a single manifold temperature must be considered. When the relative viscosities of the materials exceed a tolerable limit, or when a single manifold temperature cannot be tolerated by the materials, multimanifold dies are typically employed. In multimanifold dies, each material flows in its own manifold to the point of confluence. Each individual manifold also can be designed specifically for the rheology of each polymer resin and/or adhesive, and each manifold also can be controlled at different process temperatures.

Multimanifold dies can be designed with zero common land length so that the materials do not meet until the die lip or exit orifice. Alternatively, they can be designed with a short common flow channel such as, example, up to about 10 mm, and preferably less than about 5 mm. A zero common land would be preferred where the molten streams have extreme viscosity differences and/or temperature requirements. A short common land is generally beneficial because the period of high temperatures and high pressure while the melts are in the common land can improve the bond strength between the layers of the construction and minimize or eliminate air entrainment. In one preferred embodiment of the present invention, the manifold dies are selected so that the molten streams are joined about 1 mm before the die lip.

Referring again to Fig. 1, the unified molten structure 19 of two or more layers exits the extrusion die 17 through orifice 18, and the molten structure is deposited onto a solid substrate 21 (e.g., a release liner) supplied from a roll 20 so that the lower surface of the adhesive layer is in contact with the liner, while the upper surface of the polymeric film is in contact with air. The liner 21 is partially wrapped around the first of a three chill roll stack 22, 22A and 22B. Chill roll 22 also acts as a casting roll. The liner 21 contacts the



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surface of casting roll 22 and is interposed between the surface of the casting roll and the adhesive layer of the molten stream 19. In the embodiment illustrated in Fig. 1, the molten structure 19 is deposited on the liner 21 and the construction 23 which is formed in the process then passes over chill rolls 22A and 22B and is wound over roll 24 or wound upon itself.

The casting/cooling roll 22 and the chill rolls 22A and 22B typically are maintained at a temperature below the temperature of the unified molten structure 19 in order to cool the molten structure after it is deposited on the liner. Typically this temperature is in the range of from about 5° to about 100°C, preferably from about 20° to about 30°C.

Fig. 1A is a cross-section of the adhesive construction 23 of one embodiment of the present invention wherein the polymeric film is a monolayer. Thus, the adhesive construction 23 illustrated in Fig. 1A comprises the polymer film layer 31, an adhesive layer 30, and a release liner 21. Fig. 1B is a cross-section of an adhesive construction 23' of the present invention wherein an adhesive composition is supplied to extruder 10, and different polymer film materials are supplied to extruders 11 and 12. The resulting adhesive construction illustrated in Fig. 1B comprises polymer film layers 31 and 31A (derived from the materials supplied to extruders 11 and 12, respectively), an adhesive layer 30, and a release liner 21.

Fig. 2 illustrates another coextrusion procedure useful in preparing the adhesive constructions of the present invention. The apparatus shown in Fig. 2 utilizes four extruders 41, 42, 43 and 44 which provide four molten streams (sometimes hereinafter referred to as streams A, B, C and D, respectively) of material. Extruders 41, 42 and 43 provide molten streams 45, 46 and 47, respectively, to a feedblock 49, and extruder 44 provides a molten stream 48 of an adhesive composition directly to the die 50. As in the procedure shown in Fig. 1 and described above, the molten streams of polymer film material exiting extruders 41, 42 and 43 may be the same or different, although it is preferred, in one embodiment, that the polymeric film materials exiting extruders 41, 42 and 43 are the same. Three extruders containing the

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same polymeric film material are used to provide a coextrudate with a thicker polymeric film.

Feedblock 49 in Fig. 2 combines the molten streams of polymeric film material into a single flow channel. The feedblock 49 delivers the molten structure to the extrusion die 50 where the molten structure is combined with the adhesive stream 48, and thereafter the combined streams are reduced in height and increased in width as desired so as to provide a relatively thin and wide construction. An example of a useful feedblock is the Cloeren coextrusion feedblock available commercially from the Cloeren Company of Orange, Texas.

The discussion above, with regard to the selection of the extrusion die used in the process of Fig. 1 is applicable to the process of Fig. 2.

The unified molten structure 52 of two or more layers exits the extrusion die 50 through orifice 51, and the molten structure is deposited onto a solid substrate 54 (e.g., a release liner) supplied from a roll 53 so that the lower surface of the adhesive layer is in contact with the liner, while the upper surface of the polymeric film is in contact with air. The liner 54 is partially wrapped around the first of a three chill roll stack 55, 56 and 57. Chill roll 55 also acts as a casting roll. The liner 54 contacts the surface of the casting roll 55 and is interposed between the surface of the casting roll and the adhesive layer of the molten stream 52. In the embodiment illustrated in Fig. 2, the molten structure 52 is deposited on the liner 54, and the construction 58 which is formed in the process then passes over chill rolls 56 and 57 and is wound over roll 59 or wound upon itself.

The casting/cooling roll 55, and chill rolls 56 and 57 typically are maintained at a temperature below the temperature of the unified molten structure 52 in order to cool the molten structure after it is deposited on the liner. Typically this temperature is in the range of from about 5°C to about 100°C, preferably from about 20°C to about 30°C.

A number of additional steps optionally can be performed on the coextrudate if desired. Thus, for example, the coextrudate may be uniaxially or biaxially oriented (e.g., by heat stretching and heat setting). If it is desired to

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uniaxially or biaxially orient the coextruded adhesive constructions of the present invention, such orientation preferably occurs before the coextrudate is joined with a support material such as the release liner 21 and 54 of Figs. 1 and 2 respectively. For example, if it is desired to orient the coextrudate, the process described with regard to Figs. 1 and 2 is modified as follows. The flow of molten material into the die and/or feedblock is rearranged so that the unified molten structures 19 and 52, of Figs. 1 and 2 respectively, have the adhesive layer on top, and the molten film layer contacts the casting/chill roll 22 or 55 where the molten material is cast into a film and cooled. Chill rolls 22A and 22B in Fig. 1, and chill rolls 56 and 57 in Fig. 2 are omitted or rearranged so that the adhesive side of the cast film does not come into contact with the additional chill rolls. After the cast film has cooled, the construction may be subjected to orientation followed by lamination to the release surface of a release liner. In one preferred embodiment of the invention, the adhesive constructions are not oriented.

Machine direction or biaxial orientation of the cooled cast films of the invention prepared as described above free of a release liner can be accomplished by techniques known in the art. For example, the films can be oriented in the machine direction by using tentering frames where the clips at the edge of the tentering frame travel faster in the machine direction thereby stretching the film in the machine direction. Alternatively, the clips can be programmed to travel faster in the machine direction or to widen in the cross direction, or to stretch in both directions thereby orienting the film in both directions. When the film is to be stretched using a tenter frame, the edges of the film are preferably free of adhesive so that the clips will not stick to the film. After orientation on the tentering frame, the coextruded adhesive construction then can be laminated to a release liner.

The adhesive constructions of the present invention such as illustrated in Figs. 1A and 1B can either be collected for future printing, overlaminating, and converting at a different time and/or geographic location, or these constructions can be routed to one or more other stations for printing,

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overlaminating, and/or converting during the same operation. In an example process, the adhesive construction 23 of Fig. 1 is taken up on roll 24 and saved for future printing, overlaminating and/or conversion. Before printing, it often is desired that the exposed film surface of the adhesive construction of the invention be treated to make the exposed surface of the polymer film more receptive to subsequent printing or marking. In an example embodiment, the construction is treated by conventional surface treatment methods, such as corona treatment and the like, to increase the surface energy of the polymer film layer to facilitate wetting during the printing process.

An important feature of the adhesive constructions of the present invention is the ability to deposit printing indicia or other forms of marking on the upper surface of the film layer. Thus, the polymer film material selected for the exposed or upper surface of the adhesive constructions should be one which is receptive to printing with inks using printing techniques such as flexographic printing, screen printing, offset lithography, letter press, thermal transfer, etc., and the applied ink has acceptable adhesion to the surface of the adhesive construction.

In some instances, the properties of the very thin adhesive constructions described above can be improved by lamination of another polymeric film over the polymeric film of the coextrudate. In this embodiment, the very thin coextrudate of the invention comprising a polymeric film and the adhesive is sometimes referred to herein as a "prelaminated". Prelaminates are less than about 1 mil thick and more often from about 0.2 to 0.5 or 0.6 mil thick. This additional film over the polymer film of the prelaminated (coextrudate) generally is sometimes referred to herein and in the claims as an "overlaminated film" or "overlaminated layer", and the adhesive construction containing the overlaminated film is sometimes referred to as the "overlaminated construction" of the invention. The overlaminated film can provide additional properties such as stiffness and weatherability to the adhesive construction. The overlaminated film can also provide a transparent coating or film over printed indicia to protect the print from damage caused by physical contact with adjacent objects, and

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damage caused by exposure to moisture, water, or weather. The transparent coating can also enhance the optical quantities of the underlying printed indicia to provide a glossier and richer image. The overlaminated constructions of this invention are uniquely suited for use as labels on substrates subjected to subsequent liquid processing such as bottle washing/rinsing, filling and pasteurization, or liquid immersion (e.g., ice bath) without displaying adverse consequences such as label lifting or hazing.

The overlaminated film can be laminated to the coextruded adhesive constructions by pressure when in the form of a continuous film having a layer of adhesive material interposed between the continuous polymer film of the adhesive structure and the over laminate film. The over laminate film can be laminated to the continuous polymer film of the adhesive construction by heat and pressure without added adhesive when either the continuous polymer film or the over laminate film is formed from a material that when heat activated forms its own adhesive surface for lamination. Alternatively, the over laminate film can be applied to a curable (thermal or radiation) fluid adhesive, such as UV curable varnish. Alternatively, the over laminate film can be applied by extrusion or coating technique to the adhesive construction as a film-forming material that subsequently cures to form a continuous film. Printing indicia can be disposed on the continuous polymer film surface and/or on a backside surface of the over laminate film layer. As a further alternative, an overlaminated adhesive construction of the invention can be prepared by (a) separately coextruding two adhesive constructions, each comprising a continuous polymeric film and an adhesive layer as described above and (b) joining the two coextrudates to form a four layer structure of adhesive/film/adhesive/film. In another embodiment, an apparatus comprising four extruders such as shown in Fig. 2 (or an extruder can be added to the apparatus of Fig. 1) can be utilized with a polymer film forming material charged to the first and third extruders, and an adhesive charged to the second and fourth extruders. The result of such a coextrusion process is a film/adhesive/film/adhesive construction.

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Fig. 3 illustrates another embodiment of an overlaminated adhesive construction 40 prepared in accordance with the principles of this invention. The overlaminated adhesive construction 40 comprises the adhesive construction 23 as described above and illustrated in Fig. 1A which comprises the release liner 21, the adhesive layer 30 and the polymer film layer 31. The overlaminated construction 40 of Fig. 3 also comprises printing indicia or other form of marking 32 disposed on the polymeric film layer 31, a second adhesive layer 33 disposed over the printing indicia or marking 32, and an overlaminate film layer 34 disposed over the second adhesive layer 33. The second adhesive layer 33 can be formed from the same types of adhesive materials discussed above for the adhesive constructions of the invention.

Fig. 4 is a cross-sectional side view of another overlaminated adhesive structure 40A of the present invention. This overlaminated structure 40 comprises the adhesive construction 23' described above and illustrated in Fig. 1B which comprises the release liner 21, the adhesive layer 30, the first film layer 31, and the second film layer 31A. In addition the construction of Fig. 4 comprises a layer of printing indicia 32, a second adhesive layer 33 and the overlaminate layer 34.

It is to be understood that the overlaminated adhesive constructions of the present invention can be configured differently depending on the particular label end use. For example, the printed indicia can be interposed between the second adhesive layer 33 and the overlaminate film layer 34 in Fig. 4 (e.g., a reversed printed overlaminate film layer). Such a construction generally can be prepared by using an overlaminated film 34 that is first reversed printed and subsequently has a layer of adhesive applied to the reverse-printed surface. The overlaminated film then is laminated to the polymeric film layer 31 or 31A via the adhesive layer by conventional pressure lamination techniques.

In another embodiment, overlaminated adhesive constructions in accordance with the present invention can be prepared which are similar to the constructions illustrated in Figs. 3 and 4 except that the second adhesive layer

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33 is eliminated. In this embodiment, the overlamine film layer 34, is formed of a material that is heat activatable to provide its own adhesive surface for lamination. The material should have a sufficient "open tack" time to facilitate lamination at a relatively low temperature so as to avoid unwanted heat effects in the adhesive constructions. "Open tack" refers to the amount of time that the just activated film material remains tacky or open to adhesive contact with an adjacent surface.

The preparation of adhesive constructions in accordance with the process of the present invention is illustrated in the following examples.

#### Example 1

The apparatus utilized in this example is generally similar to the apparatus of Fig. 1 and consists of three extruders (a Killion 1" single screw extruder (stream A), a 3/4" Brabender single screw extruder (stream B), and a 27 mm Leistritz twin screw extruder in the co-rotating mode (stream C)) and a 6" Cloeren, three layer, three manifold vane die. The adhesive for the adhesive layer of the construction of the invention is fed to the Leistritz twin screw extruder having 9 heated zones which are maintained at 145°C, 155°C, 160°C, 160°C, 160°C, 160°C, 160°C, 155°C, and 155°C. The adaptor is also heated to 155°C, and the first extruder zone is unheated. Kraton D1320X is dusted with 0.1 phr of stabilizers (a 2:1 blend of Irgafos 168 and Irganox 565) and fed through the solids feed-port at the first zone at a rate of 447g/hr. Kraton LVSI-101 is heated to 120°C and fed at a rate of 57g/hr. into the fourth zone. Escorez 1310 is heated to 135°C and fed at a rate of 407g/hr. into the sixth zone. The twin screw extruder is operated at 450 rpm and requires 2.8 amps. The Brabender extruder operated at 5 rpm is charged with Unirez 2623. The temperature profile is 150°C, 155°C and 165°C in three zones with a head pressure of 600 kPa. Additional Unirez 2623 is charged to the Killion extruder operated at 5 rpm. The third zone of the Killion extruder is heated to 165°C and maintained at 1380 kPa head pressure. Molten streams from the three extruders are combined inside the Cloeren die set to a temperature of 165°C whereby the two molten streams (streams A & B) of polyamide are disposed on

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the molten stream of adhesive (stream C), and streams combine inside the die in such a manner that the adhesive containing side will contact a release liner upon exiting the die. The release liner consists of glassine paper coated with GE 7000-series silicone release on one side. The liner is partially wrapped around the bottom-most chill roll (also casting roll) of a three chill roll stack that is maintained in a closed nip position. The chill rolls are maintained at about 22°C, and the molten stream exiting the die is cast onto the liner wrapped on the bottom-most chill roll. The line speed is about 12 m/min. The resulting extrudate is about 7.5 cm. wide and about 0.5 mils (12 micron) in thickness.

#### Example 2

The procedure of Example 1 is generally followed except that Unirez 2623 is replaced by polypropylene 5E66 from Union Carbide, and the extruder temperatures and the die temperature are raised to 210°C. The Killion extruder is operated at a 5 rpm and the head pressure is 4800 kPa. The Brabender extruder is operated at 8 rpm with a head pressure of 4300 kPa. The Leistritz extruder utilizes the same temperature profile as in Example 1, and the Kraton D1320X, LVSI 101 and Escorez 2596 are handled in the same manner as in Example 1 except the feed rates are 670 g/hr, 76 g/hr and 543 g/hr, respectively. The head pressure on the Leistritz twin screw is 1310 kPa with a melt temperature of 166°C. The adhesive construction with liner is wound at 12 m/min, and the adhesive construction is about 11.5 cm wide and about 0.5 mils (12 micron) thick.

#### Examples 3-6

In these examples, the apparatus used is similar to the apparatus of Fig. 2. Two Killion 1" extruders are used for streams A and C. A Davis-Standard 1.5" extruder is used for stream B. A Leistritz twin screw extruder is used for stream D. The Killion extruders are operated at 200°C, and the Davis-Standard extruder is operated at 215°C. The Leistritz extruder is heated according to the following profile: unheated, 145°C, 160°C, 160°C, 170°C, 170°C, 175°C, 175°C, 180°C and 180°C. The adaptor is heated to 210°C. The speeds of the extruders are varied according to the product desired. The



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streams A, B and C consists of polypropylene 5E66 from Union Carbide, and these streams are fed through a feedblock into one manifold of an 11" Production Components dual manifold extrusion die. Stream D is a pressure sensitive adhesive which is fed directly into the other manifold of the extrusion dies. The extrudate is cast with adhesive in contact with a release liner, and stream A in contact with the chill roll 56. The chill roll stack is maintained at about 90°C and the die gap for the ABC layer is set to about 380 microns. The gap for the adhesive layer is about 250 microns. Additional details regarding these four examples, as well as the details of the product, are summarized in the following Table III.

Table III

	Example 3	Example 4	Example 5	Example 6
Killion rpms	5	5	2.5	2.5
Davis-Standard	4%	4%	2%	2%
Leistritz rpms	450	450	450	450
Kraton D1320X/AO g/hr	1013	253	370	1521
Kraton LVSI g/hr	95	24	38	134
Escorez 2596 g/hr	950	238	340	1426
Line speed m/min	6.1	6.1	9.1	9.1
PP film thickness (mu)	35	25	5	10
Adhesive coatweight (g/m <sup>2</sup> )	23	5	.5	24

As mentioned above, the composite constructions of the present invention may be combined with a release liner by contacting a release liner with the substrate adhesive layer to form label stock. The release liner which may be utilized in the label constructions may comprise any of a variety of materials known to those skilled in the art to be suitable as release liners. In one preferred embodiment, the release liner comprises a silicone coated paper substrate. Coated polymer film substrates also can be used as release liners.

The label stock may then be converted to labels by procedures well known to those skilled in the art. Thus, the label stock may be printed and die-cut into individual labels. The printing step may occur before or after the combining of the adhesive constructions of the invention and the release liner,

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but will precede the die-cutting of the facestock into individuals labels. The film must remain in accurate register between printing steps (for example, between successive impressions and different colors) in order that image or text may be of high quality, and between printing and subsequent die-cutting in order that the image or text be located properly on the labels. The film is under tension during printing, and may be subjected to some increase in temperature, such as, for example, when UV inks are cured, and the film must maintain dimensional stability in the machine-direction.

The label stock is die-cut into a series of spaced pressure-sensitive labels carried by the release liner. This step may be performed by rotary cutting dies in a well known manner and involves a subsequent stripping of the ladder-shaped matrix of waste or trim materials surrounding the formed labels when they are die-cut (the "rungs" of the ladder representing the spacing between successive labels). The labels then remain on the liner in spaced relation with each other. One failure mode in this operation involves poorly die-cut labels remaining with the matrix as it is stripped. In this mode, as the release levels decrease, poor die-cutting is more likely to cause labels to stay attached to the matrix material and be removed from the liner during matrix stripping along with the matrix. Another failure mode results when the films being die-cut are of insufficient strength. As the strength of the matrix material decreases, the matrix tends to tear as the matrix around the die-cut labels is pulled from the liner. The films of the present invention do have sufficient strength to avoid or reduce breakage of the matrix upstripping.

The composite constructions in one embodiment of the present invention advantageously have sufficient stiffness to be dispensable utilizing commercially available dispensable apparatus such as a peel-back edge. In a preferred embodiment of the present invention, the composite constructions are peel-plate dispensable. Dispensability, as defined earlier, includes the steps of the separation of the labels from the liner, and the successful application of the label to a substrate surface.

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The coextruded adhesive constructions of this invention are useful in a variety of applications including signs, labels, tags, decals, etc. As noted above, the constructions are particularly useful in preparing labels. The constructions also can be used as decals such as for pin striping of, for example, automobiles and trucks, especially when the constructions are very thin (e.g., faceless). When the thermoplastic elastomer adhesives described above are used in faceless constructions, the constructions exhibit reduced oozing of the adhesive around the edges, and the edging or the decal or pin stripe is less evident after application. The constructions also are useful in outdoor signs and decals for application to, for example, glass windows. The thin constructions of the invention can be die-cut, and the signs and decals can be removed from the release layer by hand. High speed dispensing (and therefore stiffness) is not an issue in these applications. Highly conformable (flexible) films such as medical films also can be prepared from the adhesive constructions of the invention. Such films which are prepared using the thermoplastic elastomer adhesives exhibit low water vapor transmission which can be further improved by selection of particular FFMs. The adhesive constructions also are useful in preparing tamper-evident labels or seals for containers such as bottles which may contain printed words such as VOID. For example, when the top of a capped bottle having a film around the top of the bottle and cap is twisted to open, the film will be pulled down on the bottle rather than fracturing and forming sharp edges.

While the invention has been explained in relation to its preferred embodiments, it is to be understood that various modifications thereof will become apparent to those skilled in the art upon reading the specification. Therefore, it is to be understood that the invention disclosed herein is intended to cover such modifications as fall within the scope of the appended claims.

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Claims

1. A die-cuttable and matrix-strippable adhesive construction comprising a coextrudate comprising:

5. A. a continuous polymeric film having an upper surface and a lower surface, and a thickness of from about 0.1 mil up to about 1 mil, and

B. an adhesive layer having an upper and lower surface wherein the upper surface of the adhesive layer is adhesively joined to the lower surface of the polymer film.

10. 2. The construction of claim 1 wherein the polymeric film (A) is a multilayer film.

3. The construction of claim 1 wherein the polymer film is selected from the group consisting of polystyrenes, polyolefins, polyamides, polyesters, polycarbonates, polyurethanes, polyacrylates, polyvinyl alcohol, poly(ethylene vinyl alcohol), polyvinyl acetates, ionomers, and mixtures thereof.

15. 4. The construction of claim 1 wherein the polymeric film (A) is a polyolefin.

5. The construction of claim 1 wherein the polymeric film (A) is a propylene polymer or copolymer.

20. 6. The construction of claim 1 wherein the polymeric film (A) has a high speed tensile strength of at least about 1 pound/inch-width.

7. The construction of claim 1 wherein the polymeric film (A) has an elongation of less than about 200%.

25. 8. The construction of claim 1 wherein the polymeric film contains at least one nucleating agent.

9. The construction of claim 1 wherein the adhesive layer comprises a pressure sensitive adhesive.

10. The construction of claim 1 wherein the adhesive layer (B) has a coat weight in the range of from about 0.5 to about 20 g/m<sup>2</sup>.

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11. The construction of claim 1 wherein the polymeric film has a hot melt viscosity that is within a factor of from about 0.07 to about 15 times the hot melt viscosity of the adhesive at the shear rates incurred during the coextrusion process.

5 12. The construction of claim 1 wherein the coextrudate has not been monoaxially or biaxially oriented.

13. The construction of claim 1 wherein the coextrudate has been oriented in the machine direction.

10 14. The construction of claim 1 wherein the coextrudate has been biaxially oriented.

15 15. The construction of claim 1 comprising, in addition to the coextrudate, a flexible substrate having a release surface wherein the release surface is in contact with the lower surface of the adhesive layer (B).

16 16. The construction of claim 1 wherein the upper surface of the polymeric film (A) has been printed with ink.

17. The construction of claim 1 also comprising an overlamine film layer disposed over the upper surface of the polymeric film (A), and printed indicia interposed between the first polymeric film (A) and the overlaminated film layer.

20 18. The construction of claim 1 wherein the adhesive layer comprises an adhesive composition comprising a thermoplastic elastomeric component and a solid tackifier resin component.

19. The construction of claim 18 wherein the adhesive composition also comprises at least one liquid rubber component.

25 20. The construction of claim 1 wherein the adhesive layer comprises a pressure sensitive adhesive composition which comprises from about 40 to about 80% by weight of a thermoplastic elastomer component and from about 20 to about 60% by weight of a solid tackifier resin component.

30 21. The construction of claim 18 wherein the thermoplastic elastomeric component comprises at least one thermoplastic elastomeric block copolymer.

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22. The construction of claim 21 wherein the thermoplastic block copolymer is selected from the group consisting of linear, branched, grafted or radial copolymers.

5 23. The construction of claim 18 wherein the thermoplastic elastomeric component of the adhesive has a melt index of less than about 10.

24. A die-cuttable and matrix-strippable adhesive construction comprising a coextrudate comprising:

10 A. a continuous polymeric film having an upper surface and a lower surface, and a thickness of from about 0.1 mil up to about 2 mils, and

B. an adhesive layer having an upper and lower surface wherein the upper surface of the adhesive layer is adhesively joined to the lower surface of the polymer film, and the adhesive comprises a thermoplastic elastomeric component and a solid tackifier resin component.

15 25. The construction of claim 24 wherein the polymeric film (A) is a multilayer film.

20 26. The construction of claim 24 wherein the polymer film is selected from the group consisting of polystyrenes, polyolefins, polyamides, polyesters, polycarbonates, polyurethanes, polyacrylates, polyvinyl alcohol, poly(ethylene vinyl alcohol), polyvinyl acetates, ionomers, and mixtures thereof.

27. The construction of claim 24 wherein the polymeric film (A) is a polyolefin.

25 28. The construction of claim 24 wherein the polymeric film has a hot melt viscosity that is within a factor of from about 0.07 to about 15 times the hot melt viscosity of the adhesive at the shear rates incurred during the coextrusion process.

29. The construction of claim 24 comprising, in addition to the coextrudate, a flexible substrate having a release surface wherein the release surface is in contact with the lower surface of the adhesive layer (B).

30 30. The construction of claim 24 wherein the adhesive composition also comprises at least one liquid rubber component.

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31. The construction of claim 24 wherein the adhesive layer comprises a pressure sensitive adhesive composition which comprises from about 40 to about 80% by weight of a thermoplastic elastomer component and from about 20 to about 60% by weight of a solid tackifier resin component.

5 32. A die-cuttable and matrix strippable pressure sensitive adhesive label construction comprising

A. a coextrudate comprising

A-1. a continuous polymeric film having an upper surface and a lower surface, and a thickness of from about 0.1 to about 1 mil,

10 A-2. a pressure sensitive adhesive layer having an upper and lower surface wherein the upper surface of the adhesive layer is adhesively joined to the lower surface of the polymeric film, and

B. a substrate having a release surface wherein the release surface is in contact with the lower surface of the adhesive layer of the coextrudate.

15 33. The construction of claim 32 wherein the polymeric film (A-1) is a multilayer film.

34. The construction of claim 32 wherein the polymer film (A) is selected from the group consisting of polystyrenes, polyolefins, polyamides, polyesters, polycarbonates, polyurethanes, polyacrylates, polyvinyl alcohol, poly(ethylene vinyl alcohol), polyvinyl acetates, ionomers, and mixtures thereof.

20 35. The construction of claim 32 wherein the polymeric film (A-1) is a polyolefin.

36. The construction of claim 32 wherein the polymeric film material of first layer (A-1) is a propylene polymer or copolymer.

25 37. The construction of claim 32 wherein the polymer film (A-1) has a melt index of less than about 10.

38. The construction of claim 32 wherein the polymeric film (A-1) has a high speed tensile strength of at least about 1 pound/inch-width.

30 39. The construction of claim 32 wherein the polymeric film contains at least one nucleating agent.

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40. The construction of claim 32 wherein the polymeric film (A-1) has an elongation of less than about 200%.

41. The construction of claim 32 wherein the adhesive layer (A-2) has a coat weight in the range of from about 0.5 to about 20 g/m<sup>2</sup>.

5 42. The construction of claim 32 wherein polymeric film layer (A-1) has a hot melt viscosity that is within a factor of from about 0.07 to about 15 times the hot melt viscosity of the adhesive at the shear rates incurred during coextrusion of the coextrudate.

10 43. The construction of claim 42 wherein the factor is from 1 to about 10.

44. The construction of claim 32 wherein the coextrudate has not been monoaxially or biaxially oriented.

45. The construction of claim 32 wherein the coextrudate has been oriented in the machine direction.

15 46. The construction of claim 32 wherein the coextrudate has been biaxially oriented.

47. The construction of claim 32 wherein the upper surface of the polymeric film (A-1) has been printed with ink.

20 48. The construction of claim 32 also comprising an overlamine film layer disposed over the upper surface of the first layer of polymeric film material (A-1), and printed indicia interposed between the polymeric film (A-1) and the overlaminated film layer.

25 49. The construction of claim 32 wherein the adhesive layer (A-2) comprises an adhesive composition comprising a thermoplastic elastomeric component and a solid tackifier resin component.

50. The construction of claim 49 wherein the adhesive composition also comprises at least one liquid rubber component.

30 51. The construction of claim 32 wherein the adhesive layer comprises a pressure sensitive adhesive composition which comprises from about 40 to about 80% by weight of a thermoplastic elastomer component and from about 20 to about 60% by weight of a solid tackifier resin component.



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52. The construction of claim 51 wherein the adhesive composition also comprises at least one liquid rubber component.

53. The construction of claim 32 wherein the thermoplastic elastomeric component comprises at least one thermoplastic elastomeric block copolymer.

54. The construction of claim 53 wherein the thermoplastic block copolymer is selected from the group consisting of linear, branched, grafted or radial copolymers.

55. A label die-cut from the coextruded adhesive construction of claim 1.

56. A label die-cut from the coextruded adhesive construction of claim 24.

57. A label die-cut from the coextruded pressure-sensitive adhesive label construction of claim 32.

58. A process for preparing a die-cuttable and matrix-strippable adhesive construction for label applications which comprises the steps of

(A) providing a removable substrate with a release surface,

(B) depositing on the release surface, a molten coextrudate comprising

(B-1) a continuous polymeric film having an upper surface and a lower surface, and a thickness of from about 0.1 mil to about 1 mil, and

(B-2) an adhesive layer having an upper surface and a lower surface wherein the upper surface of the adhesive layer is adhesively joined to the lower surface of the polymer film, and the lower surface of the adhesive layer is adhesively joined to the release surface of the removable substrate, and

(C) cooling the coextrudate.

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59. The process of claim 58 wherein the molten coextrudate is formed in a multilayer vane die, and the molten coextrudate exiting the die is self supporting until it is deposited on the release surface of the removable substrate.

5 60. The process of claim 58 wherein the molten coextrudate is formed on a multimanifold die having a common land length of from 0 to about 10mm.

61. The process of claim 58 wherein the thickness of the polymeric film (B-1) is from about 0.2 to about 1 mil.

10 62. The process of claim 58 wherein the polymeric film (B-1) is a multilayer film.

63. The process of claim 58 wherein the polymer film (B-1) is selected from the group consisting of polystyrenes, polyolefins, polyamides, polyesters, polycarbonates, polyurethanes, polyacrylates, polyvinyl acetates, ionomers, and mixtures thereof.

15 64. The process of claim 58 wherein the polymeric film (B-1) is a polyolefin.

65. The process of claim 58 wherein the adhesive layer comprises a pressure sensitive adhesive.

20 66. The process of claim 58 wherein the adhesive layer (B-2) has a coat weight in the range of from about 0.5 to about 20 g/m<sup>2</sup>.

67. The process of claim 58 wherein the polymeric film (B-1) has a hot melt viscosity that is within a factor of from about 1 to about 15 times the hot melt viscosity of the adhesive.

25 68. The process of claim 58 wherein the upper surface of the polymeric film (B-1) is subsequently printed with ink.

69. The process of claim 58 wherein an overlamine film layer subsequently is laminated over the upper surface of the polymeric film (B-1), and printed indicia are interposed between the polymeric film (B-1) and the overlaminated film layer.

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70. The process of claim 58 wherein the adhesive layer comprises an adhesive composition comprising a thermoplastic elastomeric component and a solid tackifier resin component.

5 71. The process of claim 70 wherein the adhesive composition also comprises at least one liquid rubber component.

72. The process of claim 58 wherein the adhesive layer comprises a pressure sensitive adhesive composition which comprises from about 40 to about 80% by weight of a thermoplastic elastomer component and from about 20 to about 60% by weight of a solid tackifier resin component.

10 73. The process of claim 70 wherein the thermoplastic elastomeric component comprises at least one thermoplastic elastomeric block copolymer.

74. The process of claim 58 wherein the melt index of the polymer film material of the film (B-1) is less than about 10.

15 75. A process for preparing a die-cuttable and matrix-strippable adhesive construction for label applications which comprises the steps of

(A) providing a removable substrate with a release surface,

20 (B) depositing on the release surface, a molten coextrudate comprising

(B-1) a continuous polymeric film having an upper surface and a lower surface, and a thickness of from about 0.1 mil to about 2 mils, and

25 (B-2) an adhesive layer having an upper surface and a lower surface wherein the adhesive comprises a thermoplastic elastomeric component and a solid tackifier resin component, the upper surface of the adhesive layer is adhesively joined to the lower surface of the polymer film, and the lower surface of the adhesive layer is adhesively joined to the release surface of the removable substrate, and

30 (C) cooling the coextrudate.

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76. The process of claim 75 wherein the molten coextrudate is formed in a multilayer vane die, and the molten coextrudate exiting the die is self supporting until it is deposited on the release surface of the removable substrate.

5           77. The process of claim 75 wherein the molten coextrudate is formed on a multimanifold die having a common land length of from 0 to about 10mm.

78. The process of claim 75 wherein the polymeric film (B-1) is a multilayer film.

10           79. The process of claim 75 wherein the polymer film (B-1) is selected from the group consisting of polystyrenes, polyolefins, polyamides, polyesters, polycarbonates, polyurethanes, polyacrylates, polyvinyl acetates, ionomers, and mixtures thereof.

15           80. The process of claim 75 wherein the polymeric film (B-1) is a polyolefin.

81. The process of claim 75 wherein the adhesive layer comprises a pressure sensitive adhesive.

82. The process of claim 75 wherein the adhesive layer (B-2) has a coat weight in the range of from about 0.5 to about 20 g/m<sup>2</sup>.

20           83. The process of claim 75 wherein the polymeric film (B-1) has a hot melt viscosity that is within a factor of from about 1 to about 15 times the hot melt viscosity of the adhesive.

84. The process of claim 75 wherein the upper surface of the polymeric film (B-1) is subsequently printed with ink.

25           85. The process of claim 75 wherein an overlamine film layer subsequently is laminated over the upper surface of the polymeric film (B-1), and printed indicia are interposed between the polymeric film (B-1) and the overlaminated film layer.

30           86. The process of claim 75 wherein the adhesive composition also comprises at least one liquid rubber component.

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87. The process of claim 75 wherein the adhesive layer comprises a pressure sensitive adhesive composition which comprises from about 40 to about 80% by weight of a thermoplastic elastomer component and from about 20 to about 60% by weight of a solid tackifier resin component.

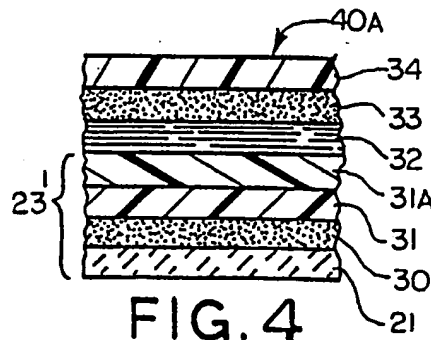
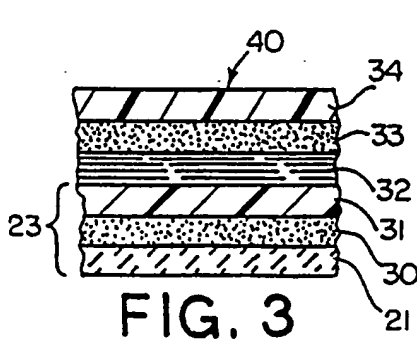
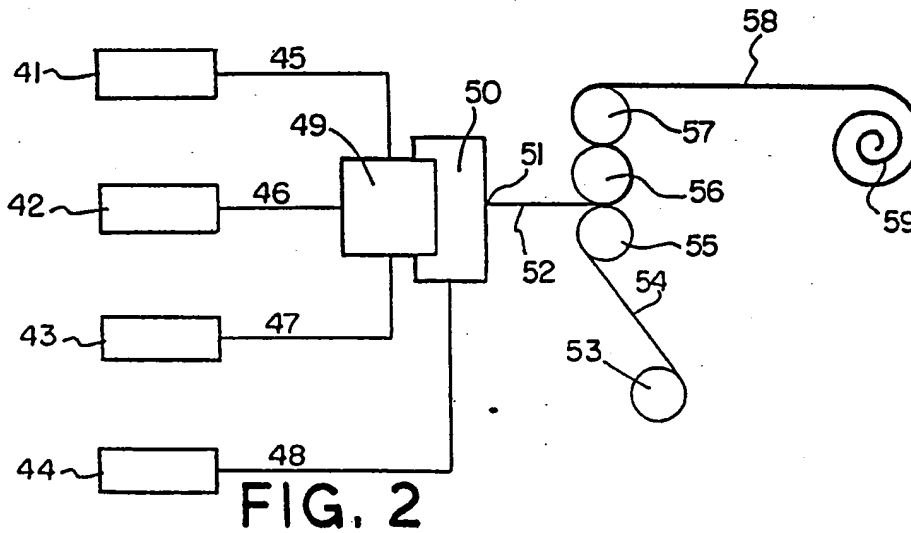
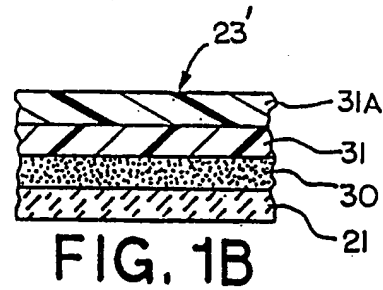
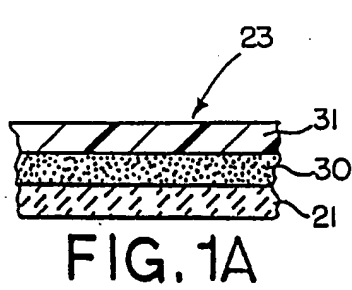
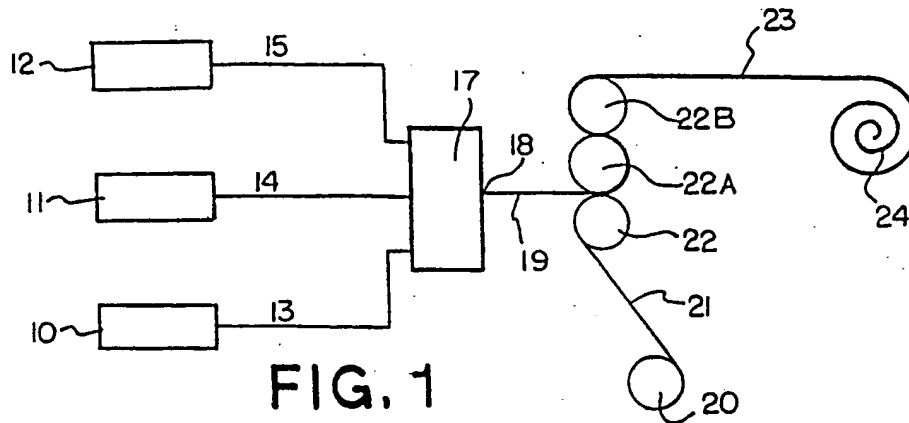
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88. The process of claim 75 wherein the thermoplastic elastomeric component comprises at least one thermoplastic elastomeric block copolymer.

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## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US99/20295

**A. CLASSIFICATION OF SUBJECT MATTER**

IPC(6) :B32B 7/12

US CL :428/40.1, 41.8, 343, 354, 355 BL, 355 AC, 356.

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 428/40.1, 41.8, 343, 347, 354, 355 BL, 355 AC, 356.

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

NONE

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

NONE

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X ----- Y	WO 96/37568 A1 (MINNESOTA MINING AND MANUFACTURING COMPANY) 28 November 1996, (28-11-96), pg 3, lines 18-26, pg 4, lines 24-29, pg 9, line 14- pg 10, line 11, Examples.	1-17, 32-48, 55, 57-69, 74 ----- 18-31, 49-54, 56, 70-73, 75-88
X ----- Y	WO 97/30844 A (ATO FINDLEY INC) 28 August 1997, (28-08-97), pg 1, lines 8-33, pg 7, line 34-pg 8, line 4, Examples.	1-17, 32-48, 55, 57-69, 74 ----- 18-31, 49-54, 56, 70-73, 75-88
Y	US 3,239,478 A, (HARLAN, Jr) 08 March 1966, (08-03-66), col 1 lines 57-62, col 2, lines 1-33, col 3, lines 47-68, col 4, lines 31-45, col 6, line 63- col 8, line 24.	18-31, 49-54, 56, 70-73, 75-88

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:	*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
*A* document defining the general state of the art which is not considered to be of particular relevance	*X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
*B* earlier document published on or after the international filing date	*Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
*L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	*A* document member of the same patent family
*O* document referring to an oral disclosure, use, exhibition or other means	
*P* document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

28 OCTOBER 1999

Date of mailing of the international search report

13 DEC 1999

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## INTERNATIONAL SEARCH REPORT

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## C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 3,932,328 A (KORPMAN) 13 January 1976 (13-01-76), Abstract, col 1, line 41-col 2 line 45, col 3, lines 36-40.	18-31, 49-54, 56, 70-73, 75-88